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Technical Report No. 3

to the

Office of Naval Research
and
Advanced Research Projects Agency
ARPA Order No. 299, Amend. 6
Contract Nonr 4511(00)
Task NR 356-464

CHEMILUMINESCENT SYSTEMS

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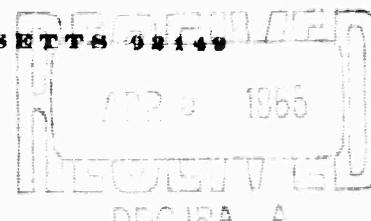
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ABSTRACT

The survey of chemiluminescent autoxidation reactions has been continued. Of the forty odd additional compounds screened, the large majority show enhanced chemiluminescence over background in potassium t-butoxide dissolved in dimethylsulfoxide (DMSO). About one-third of the reactants exceeded 1% of the standard source brightness. The latter group includes several substituted benzoins, demonstrating the generality of the chemiluminescence of the oxidation of this class of stable radicals.

The chemiluminescence of indole and several 3-substituted indoles has been investigated. In t-BuOK and DMSO solution, 5×10^{-3} M skatole is about fifty times brighter than the standard source. At a base concentration of 0.067 M the brightness is an increasing function of skatole concentration to almost 0.1 mole/liter. At this concentration the brightness is 400 times that of the standard, or about half that of 5×10^{-3} M luminol. Emission and fluorescence spectra (uncorrected) have been obtained for the basic skatole solution and for the addition, 10^{-4} M fluorescein.

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I. INTRODUCTION

In the previous report (ref. 1) initial results were given for the chemiluminescence of selected autoxidation reactions in basic aprotic media. The measurements were carried out by injection of a potassium t-butoxide (t-BuOK) solution into a solution of the autoxidizable compound in dimethylsulfoxide (DMSO) or other aprotic solvent. The initial light pulse is measured by a recording photometer (ref. 1). After decay of the initial pulse from the generally air-saturated solutions, an oxygen bubbler is turned on and the photometer current resulting from chemiluminescence is measured as a function of time.

We report here on the continuation of this survey, including further investigation of the chemiluminescence of the acyloins and indoles.

II. INSTRUMENTATION

During the past quarter the scanning photoelectric spectrometer was assembled and aligned. The instrument has been shown to have excellent sensitivity at relatively high resolution. A simple, broad band excitation unit for qualitative fluorescence measurements was constructed utilizing two GEF4T5-BLB lamps for front surface excitation. Signal-to-noise ratios > 100 were observed for the fluorescence spectrum of basic solutions of skatole in DMSO (see Section IIIB for details). The equipment for quantitative fluorescence and chemiluminescence spectral brightness is being assembled.

A tritiated phosphor source (ref. 2) has been adopted for standardization of the photometers. This procedure has the obvious advantage that results obtained at different times, or with different photometers may be meaningfully compared. The measurements of intensity of gross chemiluminescence are, therefore, presented in this report as the ratio of the photometer current produced by the sample to that produced by the "blue" phosphor source.

III. EXPERIMENTAL RESULTS

A. SURVEY OF AUTOXIDATION REACTIONS

The compounds surveyed and the results obtained during the past quarter are given in detail in Appendix 1. In Tables 1 and 2 we have assembled for convenience a cumulative summary of the brighter reactants, defined as those whose peak intensity photometer current is at least one per cent of that produced by the standard source. The nominal brightness of the source is 5 microlambert. The emission is stated to peak at 414 nm. Even neglecting geometrical factors, this ratio cannot be considered a brightness ratio for noncoincident emission spectra.

1. True Autoxidations

Table 1 lists the "bright" systems which appear to be undergoing true autoxidation reactions, as judged by, first, the requirement for oxygen and the existence of an inductive period before maximum intensity is obtained, and second the lack of sensitivity of the luminescence to purification of the reactants.

a. Acyloins

The luminescence observed for the substituted benzoins supports the view that a new class of chemiluminescent reactions has been discovered. Anisoin appears to be similar in emission intensity to benzoin, although quantitative comparisons are difficult to make in the absence of quantitative spectra. Furoin, as expected from the relative destabilization of the radical compared to benzoin, is clearly a weaker emitter. A very striking effect is noted for 4,4'-dihydroxybenzoin. The intense absorption noted for the other compounds and presumed to be that characteristic of the free radical is absent. Nevertheless, both the emission intensity and induction period are of the same order as observed for benzoin and the closely related anisoin. 2,2'-Dihydroxybenzoin which does form the dark solution has an (unsensitized) emission intensity lower by almost an order of magnitude from that of the 4,4'-isomer. Although more detailed investigation of these effects is required to understand the phenomena, one may speculate that specific resonance interactions may drastically reduce the free radical concentration in the 4,4'-compound. The decrease in self-absorption of the solution may thus balance out a sharp fall in the reaction rate of the chemiluminescent reaction.

The observed sensitivity of the peak luminescence intensity to the procedure details such as stirring, oxygen flow rate, and degree of dispersion is probably accounted for by the competing rates of the chemiluminescent reaction (presumably the oxidation of the free radical anion) which emits radiation and the overall rate of oxidation which reduces the self absorbance.

Table 1
"BRIGHT" AUTOXIDATION REACTIONS

<u>Compounds</u>	<u>Reaction Conditions^t</u>	<u>I/I₀[‡]</u>
A. Acyloins		
Benzoin*		0.10
Benzoin*	t-BuOK = 0.016	0.20
Benzoin		4×10^{-2}
Benzoin	in DMF	0.15
Benzoin	DPA	0.10
Benzoin	DPA in DMF	0.20
Benzoin	fritted gas dispersor	0.15
Anisoin		$(6.6 \pm 0.8) \times 10^{-2}$
Anisoin	DPA	0.15
4,4'Dihydroxybenzoin		2.4×10^{-2}
4,4'Dihydroxybenzoin	TP or DPA	4×10^{-2}
2,2'Dihydroxybenzoin	DPA	10^{-2}
B. Hydrocarbons		
Fluoranthene		$(5 \pm 1) \times 10^{-2}$
Fluoranthene	fritted gas dispersor	0.13
Fluorene*		1.5×10^{-2}
Fluorene*	in DMF	2.0×10^{-2}
C. Indoles		
Indole	0.067 t-BuOK	0.30
Skatole		60.0
D. Ketones		
9-Fluorenone*	in DMF	3×10^{-2}
Benzil*		1×10^{-2}

* Previously reported.

† Reaction conditions are 5×10^{-3} M in 0.1 M t-BuOK in DMSO unless otherwise noted. Sensitizers are 10^{-4} M. Abbreviations are as follows:

DMF = dimethylformamide

DMSO = dimethylsulfoxide

DPA = 9,10-diphenylanthracene

TP = p-terphenyl

‡ Ratio of photometer current, I, to that produced by standard source, I_0 .

Table 2
"BRIGHT" INITIAL FLASH REACTANTS*

<u>Compounds</u>	<u>Reaction Conditions†</u>	<u>I/I₀‡</u>
A. Previously Reported (ref. 1)		
2-Benzylimidazoline·HCl	see below	0.6
Benzaldehyde		2×10^{-2}
Dibenzothiophene		$\approx 3 \times 10^{-2}$
o-Anisidine	TP or TPB	$\approx 2 \times 10^{-2}$
Phthalidamide	TPB	1×10^{-2}
o-Dimethylhydrazine		2×10^{-2}
B. Not Previously Reported		
Furoin		1.5×10^{-2}
3(N-R formimidoyl) indoles:		
R=phenyl		1×10^{-2}
R=2-thiazoyl		4×10^{-2}
R=2-pyridyl		1×10^{-2}
Indene		1×10^{-2}
Indane		1×10^{-2}
Indane	DPA, TP or RUB	3×10^{-2}
Cinnamaldehyde		0.15
Cinnamaldehyde	TPB	0.34
Cinnamaldehyde	TP	0.20
Benzylimidazoline·HCl		1×10^{-2}
Hydrazine dihydrochloride		2×10^{-2}
Benzhydrol	RUB	1×10^{-2}
Isophthalic acid		2×10^{-2}
Isophthalic acid	TPB or TP	$3.5 \pm 0.5 \times 10^{-2}$
Anthraquinone		2×10^{-2}
Anthraquinone	TPB or TP	3×10^{-2}
2-Naphthol		2×10^{-2}
Benzamide	DPA	1×10^{-2}
Benzamide	TPB	2×10^{-2}
Salicylhydrazide	-TP	1×10^{-2}
Salicylhydrazide	DPA	$> 2 \times 10^{-2}$
Salicylhydrazide	TPB	4×10^{-2}
"1-Nitroso-2-naphthol"	(pract.)	8×10^{-2}

* For compounds not already listed in Table 1.

† Reaction conditions are 5×10^{-3} M in 0.1 M t-BuOK in DMSO unless otherwise noted. Sensitizers are 10^{-4} M. Abbreviations are as follows:

DMF = dimethylformamide DMSO = dimethylsulfoxide
 DPA = 9,10-diphenylanthracene TP = p-terphenyl
 TPB = tetraphenylbutadiene RUB = rubrene

‡ Ratio of photometer current, I, to that produced by standard source, I_0 .

In summary, we have shown that acyloin oxidation, at least for fairly well resonance-stabilized structures, leads generally to chemiluminescence and that relatively simple structural variation may lead to striking modification of system behavior. Much further work is required to elucidate this behavior in detail in order to isolate relatively efficient chemiluminescent reactions.

b. Indoles

(1) Chemiluminescence of Skatole

Upon being informed by Professor F. H. Johnson that Dr. Totter (ref. 3) had observed that skatole was the brightest of the indoles tested in DMSO and aqueous KOH, we compared the emission to that obtained in the aprotic solvent DMSO and t-BuOK. The results are given in Table 3. The decay half-life for the conditions above was approximately constant at 290 ± 10 seconds. The increase in brightness observed in the nonaqueous solvent is apparent.

Table 3

SKATOLE LUMINESCENCE IN AQUEOUS DMSO

(skatole = 3×10^{-3} m/l)

<u>Solvent, vol-% H₂O</u>	<u>Base Concentration, m/l</u>	<u>I/I₀</u>	<u>Remarks</u>
11	0.55 KOH	9	probably two-phase
2	0.067 KOH	14	
0	0.067 t-BuOK	60	

The dependence of the skatole peak emission intensity upon skatole concentration at a fixed base concentration is shown in Figure 1. At these conditions deviation from linearity occurs at concentrations greater than $\approx 2 \times 10^{-2}$ M. Investigation of the base dependence of the peak emission intensity at 5×10^{-3} M skatole reveals that the peak intensity rises with base concentration until a 1:1 mole ratio is attained. The intensity then remains constant and begins to decline again at high base concentrations (> 0.1 M).

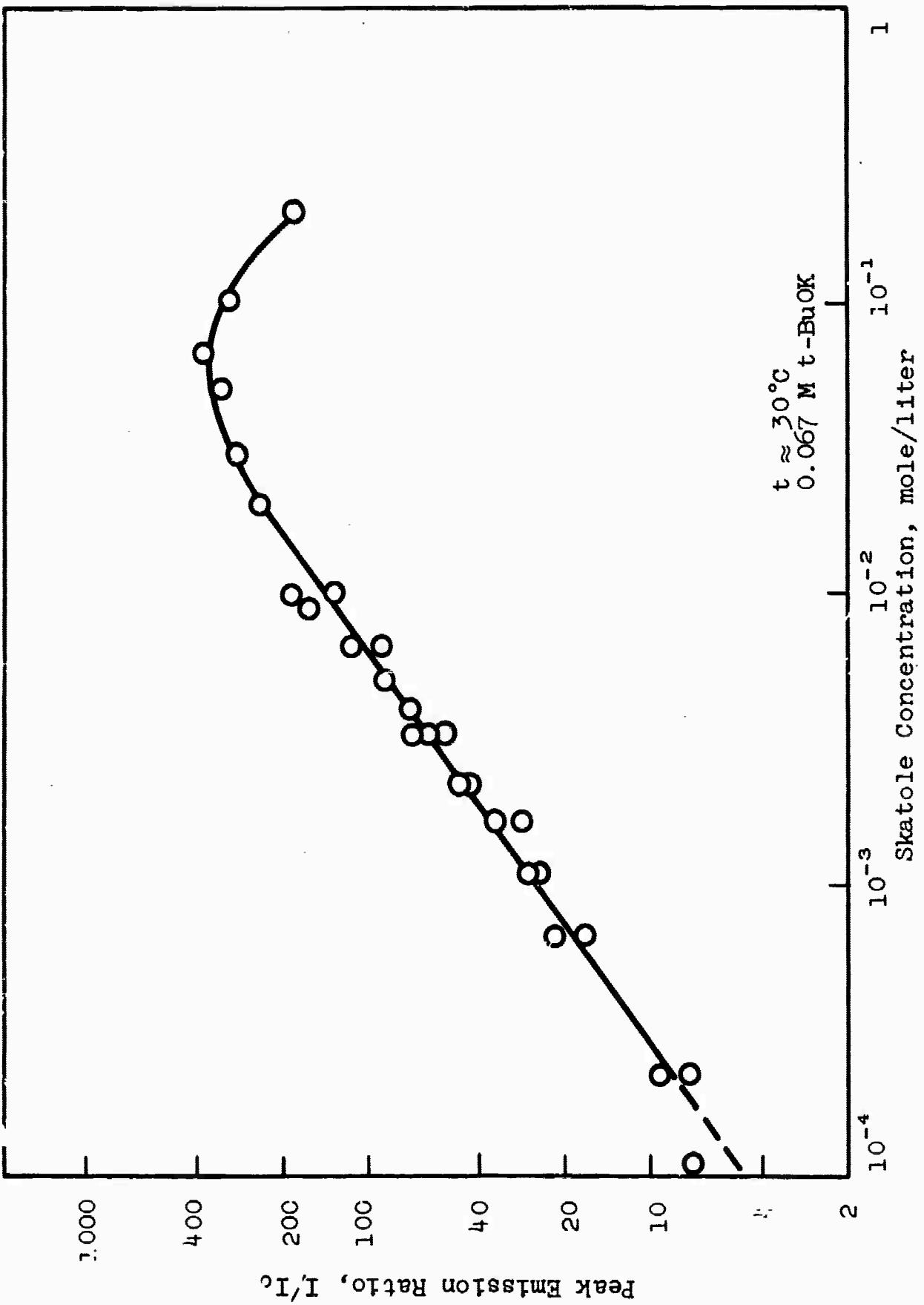
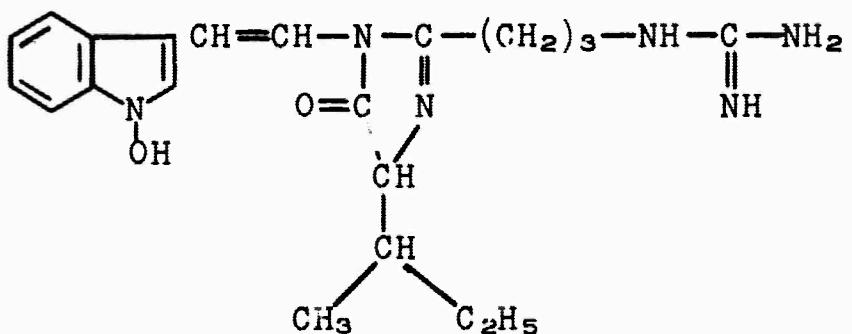


Figure 1. Peak Emission Intensity for Skatole Autoxidation in DMSO
As a Function of Skatole Concentration

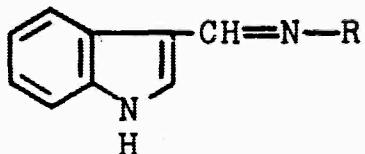
Preliminary measurements made at high skatole concentration with high base concentrations indicate very little change in the shape of the emission peak vs concentration curve of Figure 1. It appears, therefore, that the departure from linearity observed is to be attributed to concentration quenching since self absorption by reactants or products is small.

(2) Related Indoles

We have examined several 3-substituted indoles (available to us from another program) since they are structurally related to the tentative structure assigned to Cypridina luciferin (ref. 4), viz.,



The indoles investigated have the structure



where R is an aromatic substituent. The oxidation peak emission for these 3(N-R formimidoyl) indoles is found to be more than two orders of magnitude below that of indole.

(3) Chemiluminescence and Fluorescence Spectra

We have obtained preliminary emission and fluorescence spectra for skatole in t-BuOK and DMSO solution. The data reported are qualitative only, since the required calibrations and corrections have not yet been carried out. The gross emission spectrum for 10^{-2} M skatole in 0.067 M t-BuOK in DMSO three minutes after oxygen bubbling commenced is shown in Figure 2, curve B. The scan rate was ≈ 220 nm/min. Since the decay half-life under these conditions exceeds five minutes and the peak half-intensity width is ≈ 75 nm, little shape distortion is introduced by the chemical decay. The uncorrected emission peak is at 489 nm.

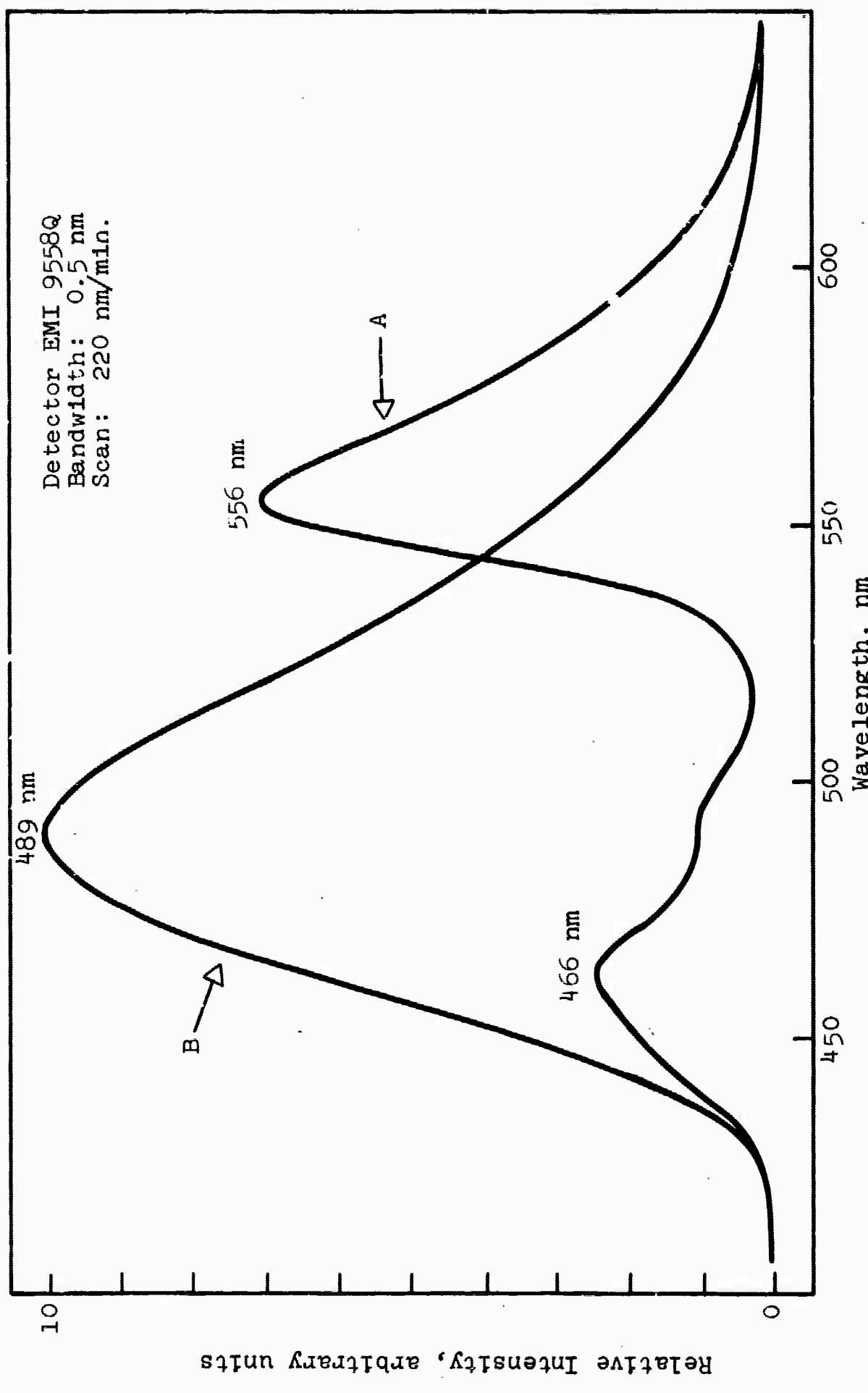


Figure 2. Chemiluminescence Spectra of Skatole Autoxidation in DMSO (uncorrected). Skatole 10^{-2} M, t-BuOK 0.067 M. Scan started after peak emission attained. Sample depth 2.5 cm. Curve A with 10^{-4} M fluorescein; Curve B unsensitized.

The uncorrected fluorescence emission for an aged, initially air-saturated solution of 10^{-2} M skatole in 0.067 t-BuOK (taken in different geometry) is found to peak at 474 nm.

In Figure 2, curve A, is also presented the emission spectrum for skatole in the presence of 10^{-4} M fluorescein at two minutes after oxygen turn-on. In addition to the major fluorescence emission peak at 555 nm the shortwave emission peak is observed at 466 nm (with a shoulder at 489 nm). These features are rather well reproduced in the fluorescence spectrum of an identical fluorescein-skatole solution (taken in the absence of oxygen). The major fluorescence peaks occur at 548 and 461 nm. Since this emission (at 466 in chemiluminescence and 461 in fluorescence) appears in neither pure fluorescein nor pure skatole it appears most likely to be the tail of the skatole emission modified by fluorescein absorption. Since both curves of Figure 2 were taken under identical conditions they may be directly compared, but only at the same wavelengths.

We have, therefore, demonstrated only that a wavelength shift is readily obtained in the reaction. To determine whether true energy transfer occurs (i.e., sensitized emission leading to increased quantum efficiency) or merely "trivial" fluorescence (i.e., absorption and reradiation with no increase of quantum efficiency) we must await calibration of the instrumentation.

c. Hydrocarbon Autoxidation

The peak chemiluminescence intensity of the autoxidation of the condensed aromatic hydrocarbon fluoranthene has been found to be comparable to that of benzoin. As for benzoin, no decrease of luminescence is observed upon purification. In this case the product species are highly absorbing. Although it is tempting to relate this reaction to the electron-transfer luminescence reactions recently studied (ref. 5), many possible reaction paths clearly exist. Further investigation, including elementary structural variation, appears desirable.

2. Bright "Flash" Reactions

In Table 2 are listed those reactants which are distinguished by their initial luminescence "flash" and are not already listed in Table 1. That is, any luminescence during autoxidation does not attain the arbitrary level of 1% of the standard.

It might be expected that several different classes of reactants may be found in this category. As a result of the fairly rapid mixing at injection, trace oxidants such as peroxides present as impurities, may rapidly attack the class of substance undergoing inefficient chemiluminescent autoxidation. Thus furoin gives a bright initial flash on mixing generally larger than the subsequent autoxidation peak. In the presence of tetraphenylbutadiene,

the initial flash exceeds the brightness level for inclusion in Table 2.

Another group is represented by compounds which appear to contain chemiluminescent impurities at low concentrations. An Eastman "practical" grade of 1-nitroso-2-naphthol (NN) has been found to produce a bright flash, which is reduced in intensity by recrystallization by an order of magnitude. The residue, on the other hand, yields an increased emission intensity. Efforts are under way to identify the active species. 2-Benzylimidazoline hydrochloride has been found to give an initial flash which varies over two orders of magnitude and is dependent as well on the source of supply.

Finally the flash produced by compounds which are known to be sensitive to peroxidation induced condensations, of which cinnamaldehyde is an outstanding example, clearly require detailed investigation to isolate the active species.

In summary, a considerable number of reactions exist which provide promising clues to the existence of possible chemiluminescent reactions of high efficiency as shown by their relative brightness at (presumably) low concentrations. The major problem to be solved is the determination of the identity of the reactant species.

IV. FUTURE WORK

A. INSTRUMENTATION

The most urgent requirement is the energy calibration of the scanning spectrometer and completion of the quantitative fluorescence apparatus. This will permit determination of chemiluminescence and fluorescence brightness in the meaningful units of photons/cm³ - unit bandwidth and permit computation of the fundamental quantum efficiencies.

We propose to carry out phototube calibration by substitution of an energy calibrated thermopile and overall instrument calibration by use of fluorescent and chemiluminescent standards in fixed geometry.

B. RESEARCH OBJECTIVES

The objectives for the remainder of this contract period are:

1. Determination of the spectral brightness for selected acyloins, indoles, and selected additional "bright" species.
2. Determination of fluorescence quantum efficiencies for the above-selected species under reasonably optimum conditions.
3. Determination of near-optimum reaction parameters for skatole oxidation, including investigation of sensitizer, solvent and reaction catalysts.
4. Continuation of the chemiluminescence survey for selected substrates. In Appendix 2 is given an additional listing of compounds now on hand retrieved from the Monsanto Company file selected for the survey.

V. REFERENCES

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2. Luminous Products Corp., Boston, Mass., Model NEP-1.
3. "Chemical and Enzymatic Studies on the Conversion of Chemical Energy to Light", Final Tech. Report, Contract AF-AFOSR-62-73 and AF-AFOSR-44-63, G. E. Philbrook, University of Georgia, June 1964, AD 602798.
4. Y. Hirata, et al, Tetrahedron Letters, 5, 4 (1959).
5. E. A. Chandross and F. I. Sonntag, J. Am. Chem. Soc., 86, 3179 (1964).

Appendix 1
AUTOXIDATION REACTIONS

No.	Compound and Structure	Run	Sensitizer*	Initial Pulse ratio	Peak O_2 Current ratio	Time to O_2 Peaks	Appearance		Comments
							Before O_2 Add.	After O_2 Add.	
1	p-Benzoquinone	a b	DPA	2.0x10 ⁻³ 2.6x10 ⁻³	10 ⁻⁴ 10 ⁻⁴	4.5 min 3 min	dk brn	dk brn	
2	Isophthalic acid	a b c d	DPA TPB TP TP	2x10 ⁻² >2x10 ⁻² 4x10 ⁻² 3x10 ⁻²	4x10 ⁻⁴ 4x10 ⁻⁴ 6x10 ⁻⁴ 6x10 ⁻⁴	20 sec 5 sec 25 sec	orange-yellow orange-yellow yellow yellow	orange-yellow orange-yellow yellow yellow	
3	Anthraquinone	a b c d	DPA TPB TP TP	2x10 ⁻² 2x10 ⁻² 3x10 ⁻² 3x10 ⁻²	1x10 ⁻⁴ 7x10 ⁻⁴ 1.0 ⁻³ 7x10 ⁻⁴	80 sec 30 sec 25 sec 45 sec	rd org orange orange orange	rd org orange orange orange	
4	2 Naphthol	a b	DPA	2x10 ⁻² 1.6x10 ⁻²	5x10 ⁻⁴ 7x10 ⁻⁴ 2x10 ⁻⁴ 7x10 ⁻⁴	5 sec 25 min 5 sec 10 min			two oxidation peaks with O_2 secondary peak secondary peak no effect with sensitizer
5	Benzoin	e b c d e	DPA DPA DMSO DMSO DMSO	10 ⁻³ 10 ⁻³ 5x10 ⁻⁴ 7x10 ⁻⁴ 10 ⁻³	(1.2±0.2)x10 ⁻¹ 2x10 ⁻¹ 4x10 ⁻² 1x10 ⁻¹ 0.15	62±2 sec 57 sec 4 min 50 sec 2 min 20 sec 14 sec	yellow yellow yellow yellow yellow	solvent DMF solvent DMSO solvent DMSO solvent DMSO recrystallized, fritted dispersor	

NOTE: See end of Table.

Appendix 1 (Continued)
AUTOXIDATION REACTIONS

No.	Compound and Structure	Run	Sensitizer*	Initial Pulse ratio	Peak Off Current ratio	Time to O_2 Peak*	Appearance		Comments
							Before O_2 Add.	After O_2 Add.	
6	Duroquinone 	a b	DPA TPB	5x10 ⁻⁴ 3x10 ⁻⁴	1.7x10 ⁻³ 1.7x10 ⁻³	6M, 20S 7 min	dk rd dk rd	dk rd dk rd	brn No effect with sensitizers
7	Phloroglucinol 	a b	DPA TPB	1x10 ⁻³ 1x10 ⁻³	3x10 ⁻⁴ 2x10 ⁻⁴ 6x10 ⁻⁴	1.3M, 40S 15 min 3M, 153	clear yellow yellow	cloudy yellow	With fluorescent surface
8	2-Nitrofluorene 	a		10 ⁻⁴	10 ⁻⁴	16 min	deep green violet	reddish violet	lower than blank
9	2-Furamide 	a b	DPA	>2x10 ⁻³ 4x10 ⁻³	4x10 ⁻⁴ 3x10 ⁻⁴	6 sec 11.5 min	clear yellow	clear yellow	
10	Benzamide 	a b c d	TP DPA TPB	>6x10 ⁻³ >2x10 ⁻² 10 ⁻² 2x10 ⁻²	6x10 ⁻⁴ 2x10 ⁻³ 10 ⁻³ 1.6x10 ⁻³	1.5 sec 25 sec 35 sec 15 sec	yellow yellow yellow yellow		

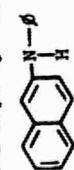
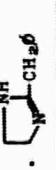
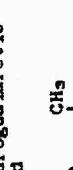
NOTES: See end of Table.

Appendix 1 (Continued)
AUTOXIDATION REACTIONS

No.	Compound and Structure	Run	Sensitizer	Initial Pulse Ratio	Peak O ₂ Current ratio	Time to O ₂ Peak	Appearance		Comments
							Before O ₂ Add.	After O ₂ Add.	
11	 Salicylhydrazide	a	TP	>>2x10 ⁻³	5x10 ⁻³	30 sec	yellow	greenish yellow	
		b	TP	1x10 ⁻²	2x10 ⁻³	5 min	yellow	yellow	
		c	DPA	>2x10 ⁻²	5x10 ⁻³	4 min	yellow	greenish yellow	O ₂ signal persists for ~4 min.
		d	TPB	4x10 ⁻²	4x10 ⁻³	3M, 15S	yellow	greenish yellow	O ₂ signal persists for ~4 min.
12	 Oramide	a	TP	>2x10 ⁻³	2x10 ⁻⁴	30 sec	lt yellow	yellow	precipitate
		b	DPA	>2x10 ⁻³	1.5x10 ⁻⁴	20 sec	lt yellow	orange-yellow	no precipitate
		c	TP	6x10 ⁻³	3x10 ⁻⁴	5 sec			
13	 Hydroquinone	a		1.5x10 ⁻⁴	6x10 ⁻⁴	5 min	brownish-orange	brownish-orange	
		b		1x10 ⁻³	6x10 ⁻⁴	2M, 40S	brownish-orange	brownish-orange	O ₂ flowing when base was injected.
		c	TP	>6x10 ⁻⁴	5x10 ⁻⁴	5 min			
14	 1-Nitroso-2-naphthol	a		(9.0+0.8)x10 ⁻²	(3±1)x10 ⁻⁴	~5 sec	deep green	visible yellow	emission with base injection.
		b		(1.1+0.0)x10 ⁻²	(1.4+0.6)x10 ⁻⁴	<5 sec	brownish-red	brownish-red	"Practical Grade" Recrystallized.
15	p-Nitrosophenol Sodium Salt	a		5x10 ⁻⁴	2x10 ⁻⁴	20 min	green		

NOTES: See end of Table.

Appendix 1 (Continued)
AUTOXIDATION REACTIONS

No.	Compound and Structure	Run	Sensitizer*	Initial Pulse ratio		Peak Ost Current ratio	Time to O ₂ Peak#	Appearance		Comments
				O ₂ Add.	O ₂ Add.			Before O ₂ Add.	After O ₂ Add.	
15	N-phenyl-2-naphthylamine a 	a		1.5x10 ⁻³		1x10 ⁻⁴	20 sec	orange	dk brn	
16										
17	2-Benzylimidazole-HCl b 	b		6x10 ⁻³		10 ⁻³	6 min			Aldrich Columbia
18	Pyrocatechol 			10 ⁻³		2x10 ⁻⁴	20 min			
19	Benzalazine ρ -N=N- ρ			6x10 ⁻⁴		6x10 ⁻⁵	16 min	yellow	rd-brn	No oscillations
20	Nordihydroguaiaretic acid 	a		6x10 ⁻³		2x10 ⁻⁴	8 min	orange		
		b	TP	5x10 ⁻³		2x10 ⁻⁴	9 min	orange		
		c		2.5x10 ⁻³						
21	Triphenylamine ρ_3N	a		2x10 ⁻³		3x10 ⁻⁴	16 min	yellow	orange	
		b	DPA	5x10 ⁻³		3x10 ⁻⁴	21 min	yellow	orange	
		c	TP	2.5x10 ⁻³		2x10 ⁻⁴	18 min	yellow	orange	

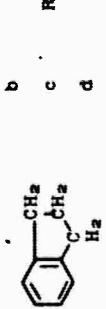
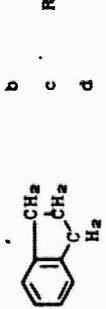
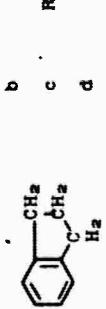
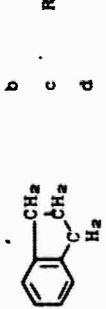
NOTES: See end of Table.

Appendix 1 (Continued)
AUTOXIDATION REACTIONS

No.	Compound and Structure	Run	Sensitizer ^a	Initial Pulse Ratio	Peak Off Current ratio	Time to O ₂ Peak*	Appearance		Comments
							Before O ₂ Add.	After O ₂ Add.	
22	Indene	a		10 ⁻²	1.5x10 ⁻³	20 sec	yellow	blackish	
		b	DPA	10 ⁻²	1x10 ⁻³	10 sec	yellow	blackish	No effect with sensitization.
		c	TP	10 ⁻²	1.5x10 ⁻³	30 sec	yellow	blackish	No effect with sensitization.
		d	TPB	1.3x10 ⁻²	1.5x10 ⁻³	50 sec	yellow	blackish	No effect with sensitization.
23	Fluoranthene	a		1.5x10 ⁻³	4x10 ⁻²	50 sec	yellow	blue-purple	
		b	DPA	1.5x10 ⁻³	4x10 ⁻²	35 sec	yellow	blue-purple	No apparent effect with sensitization.
		c	TP	1.5x10 ⁻³	3x10 ⁻²	40 sec	yellow	blue-purple	No apparent effect with sensitization.
		d	TPB	1.5x10 ⁻³	3x10 ⁻²	40 sec	yellow	blue-purple	No apparent effect with sensitization.
		e	Rubrene	1x10 ⁻³	2.5x10 ⁻²	2 min	yellow	reddish	No apparent effect with sensitization.
24	Fluoranthene (recrystallized)	a		1.5x10 ⁻³	6x10 ⁻²	50 sec	dp purple	dp purple	Fritted dispersor.
		b		6x10 ⁻³	1.7x10 ⁻¹	10 sec			
		c	DPA	2x10 ⁻²	1.7x10 ⁻²	50 sec			
		d	Rubrene	1.5x10 ⁻³	2.5x10 ⁻²	90 sec			
		e	TP	1.7x10 ⁻³	6x10 ⁻²	50 sec			
		f	TPB	1.5x10 ⁻³	4x10 ⁻²	30 sec			
25	Triphenylmethane β ₂ CH	a		10 ⁻³	2.5x10 ⁻⁴	19 min			
26	Bluet	a		2x10 ⁻³	3x10 ⁻⁴	20 min			
									H ₂ NCONHC ₂ ONH ₂

NOTES: See end of Table.

Appendix 1 (Continued)
AUTOROXIDATION REACTIONS

No.	Compound and Structure	Run	Sensitizer*	Initial Pulse ratio	Peak Off Current ratio	Time to O ₂ Peak*	Appearance		Comments
							Before O ₂ Add.	After O ₂ Add.	
27	 Indane	a		10 ⁻²	1.2x10 ⁻⁴	20 sec	yellow	yellow	Second peak at ~16 min.
		b	DPA	3x10 ⁻²	1.2x10 ⁻⁴	16 min			
		c	Rubrene	2.5x10 ⁻²	1.2x10 ⁻⁴	20 sec			Second peak at ~16 min.
		d	TP	3x10 ⁻²	3x10 ⁻⁴	16 min			Second peak at 18 min.
		e	TPB		3.5x10 ⁻⁴	2 sec			Second peak at 21 min.
28	 Furolin	a		8x10 ⁻³	3x10 ⁻³	5 sec, 40S	brownish	brownish	
		b	DPA	3x10 ⁻³	3x10 ⁻³	4M, 10S	yellow	yellow	
		c	Rubrene	7x10 ⁻³	10 ⁻³	10 min	dark blue	dark blue	
		d	TP	6x10 ⁻³	10 ⁻³	13.5M			
		e	TPB	1.5x10 ⁻²	1.5x10 ⁻³	12 min			
29	 (N-phenylformimidoyl)indole	a		~10 ⁻²	5x10 ⁻³	45 min			
		b	DPA	6x10 ⁻³	6x10 ⁻³	13 min			
		c	TP	6x10 ⁻³	5x10 ⁻³	25 min			
30	 (N-2-thiisoylformimidoyl)indole	a		4x10 ⁻²	1x10 ⁻³	5 sec			
		b		1.5x10 ⁻²	2x10 ⁻³	5 sec			
		c	Rubrene	3.7x10 ⁻²	1.5x10 ⁻⁴	5 sec			
		d	DPA	3.6x10 ⁻²	3x10 ⁻³	6 min			
		e	TPB	4.2x10 ⁻²	2x10 ⁻³	6 min			

NOTES: See end of Table.

APPENDIX 1 (Continued)

No.	Compound and Structure	Run	Sensitizer*	Initial Pulse ratio	Peak Off Current ratio	Time to $\frac{1}{2}$ Peak	Before $\frac{1}{2}$ Add.	After $\frac{1}{2}$ Add.	Comments
31	<chem>NC1=CC=C(C=C1)C(=O)N</chem> 3-(N-2-Pyridyl-formimidoyl)-indoles	a b c d	Rubrene TP TPB	$\sim 10^{-8}$ 8×10^{-3} 7×10^{-3} 1.3×10^{-2}	4×10^{-3} 3×10^{-3} 3×10^{-3} 3.5×10^{-3}	20 min 3 min 14 min 3 min	0.08 SCPN. Instead of O ₂ SCPN. 0.08 SCPN. Instead of O ₂ SCPN. 0.08 SCPN. Instead of O ₂ SCPN.	0.08 SCPN. Instead of O ₂ SCPN. 0.08 SCPN. Instead of O ₂ SCPN. 0.08 SCPN. Instead of O ₂ SCPN.	
32	<chem>N#Cc1ccccc1</chem> H ₂ N—NH ₂ ·2HCl	a b c d	DPA Rubrene TP	2×10^{-2} 10^{-8} 6×10^{-3} 6×10^{-3}	10^{-3} 6×10^{-4} 3×10^{-4} 3×10^{-4}	15 sec 5 sec 5 sec 5 sec	Second peak = same height as first peak at t = 20 min.	Second peak = same height as first peak at t = 20 min.	
33	<chem>CC(O)C</chem> Benzhydrol	a b c	Rubrene DPA	2×10^{-3} 1.2×10^{-2}	2×10^{-4} 8×10^{-4}	20 min 20 min	Peak signal increased spontaneously: O ₂ had little immediate effect.	Peak signal increased spontaneously: O ₂ had little immediate effect.	
34	<chem>CC(=O)C</chem> Cinnamaldehyde	a b c d e	DPA TP TPB Rubrene	1.5×10^{-1} 1.5×10^{-1} 2×10^{-1} 3.4×10^{-1} $.5 \times 10^{-1}$	4×10^{-4} 5×10^{-4} 7×10^{-4} 7×10^{-4} 7×10^{-4}	11 min 10 min 5 sec 5 sec 15 sec	reddish reddish reddish reddish red	reddish reddish reddish reddish red	
35	<chem>CC(=O)C</chem> 4-Hydroxy-4-methyl-2-pentanone			10	2×10^{-3}	6 min			
36	<chem>CC(=O)C</chem> 1,3-Dihydroxy-2-propanone			10^{-4}	1.5×10^{-4}	12 min	No enhanced chemiluminescence.		

NOTES: See end of Table.

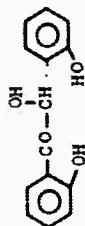
Appendix 1 (Continued)
AUTOXIDATION REACTIONS

No.	Compound and Structure	Run	Sensitizer*	Initial Pulse ratio	Peak O_2^+ Current ratio	Time to O_2^+ Peak	Appearance		Comments
							Before O_2 Add.	After O_2 Add.	
37	Indole								
38	Skatole								
		a b c	Fluorescein						
39	Diphenylamine β -NH	a b	DPA	4×10^{-3}	7×10^{-3} 6×10^{-3}	2.5 sec 15 sec	dk green	Fritted dispersor.	
40	Anisoin	a	DPA TP	10^{-3} 2×10^{-3} 10^{-3}	$(6.6 \times 0.8) \times 10^{-2}$ 0.15 6.6×10^{-2}	20 sec 23 sec 24 sec	same color sequen-	Fritted gas dispersor.	
		b c					ce as benzoin		
41	Tetraphenylhydrazine β -N - \bar{N} β ₂	a b	DPA	2×10^{-3}	3×10^{-3} 7.4×10^{-3}	3.5 min 17 sec		Fritted gas dispersor	
42	4,4'-Dihydroxybenzoin	a b	DPA + RUB	2.4×10^{-3} 4×10^{-3}	2.4×10^{-2} 2.6×10^{-2}	30 sec 40 sec		Fritted gas dispersor.	
		c d	TF DFA	6×10^{-3} 7×10^{-3}	4×10^{-2} 4×10^{-2}	60 sec 60 sec	Does not form dark solution in base.		

NOTE 3: See end of Table.

Appendix 1 (Continued)
AUTOXIDATION REACTIONS

No.	Compound and Structure	Run	Sensitizer*	Initial Pulse ratio	Peak Off Current ratio	Appearance		Comments
						Before O ₂ Add.	After O ₂ Add.	
43	2,2'-Dihydroxybenzoin	a	DPA	1.8x10 ⁻² 2x10 ⁻²	4.5x10 ⁻³ 10 ⁻²	18 sec	15 sec	Fritted dispersor. Color sequence similar to benzoin.



NOTES: * Abbreviations

DPA = 9,10-Diphenylanthracene
TP = p-Triphenyl
TPB = Tetraphenylbutadiene
RUB = Rubrene

† Ratio of photometer current to photometer current produced by standard source.

* S = second, M = minute

Reaction Conditions

All compounds 5x10⁻³ M in 0.1 M t-BuOK in DMSO;
Sensitizers 10⁻⁴ M unless otherwise noted.

APPENDIX 2

SAMPLES RETRIEVED FROM MONSANTO COMPANY SRC FILE FOR SCREENING PROGRAM

1,4 Bis(dimethyldithiocarbamoyl)but-2-yne
Tetrahydro-2-thio-2H-1,3-thiazine
Oxazolidine-2-thione
N-Isopropyltrifluoroacetamide
Phenyl(phenylcarbamoyl)phosphinic acid
Ethyl hydroxy carbamate
Ethyl 2-cyano-3-(4-diethylaminophenyl)acrylate
N,N-Methylphenyl-N'-benzenesulfonylformamidine
1-Methyl-1-phenyl-2-sulfinylhydrazine
3,7-Thiaxanthenediamine-5,5-dioxide
5-Methyl-3(beta pyridyl)1,2,4-oxadiazole
2,5-Bis(4-methoxyphenyl)-thiazolo[5,4-d]thiazole
Disemicarbazone of 2,2,4,4-Tetramethylcyclobutanedione
4-Hydroxy-2-benzoxazolethiol
1-Methyl-2-acetylmino-5(4-methoxybenzylidene)4-imidazolidinone
Triphenylphosphoranylidene-2-propanone
2,3-Epoxy-2,3-dihydro-1,4-naphthoquinone
alpha-Cyanoacetamide
Thianaphthene
alpha chloro-gamma-hydroxyacetoacetic acid gamma lactone
4-Hydroxycoumarin
1,3-Di-p-tolyluretidine
Triphenylphosphine-p-toluenesulfonylimine
Tris(p-dimethylaminophenyl)phosphine-p-toluenesulfonylimine
Lactic Acid hydrazine
S,S-di-n-butyl-N-(phenylsulfonyl)sulfilimine
2-(2-Hydroxyethyl)-5-phenyl-2,4-pentadienoic acid gamma lactone
3-(1-Hydroxy-N-phenylformimidoyl)acrylic acid gamma lactone
alpha-(2-Hydroxyethyl)-p-methoxycinnamic acid gamma lactone
5(o-Chlorophenyl)hydantoin
alpha Benzylthiocinnamide
N-Anilinophthalimide
2,4-Dimethoxybenzylidenemalonitrile
Difurfuryl vinylene dicarbamate
L-carvone
10,10'Bianthrone
2,5-Diphenyl 1,3,4-oxadiazole
1,4,7-Tris(p-tolylcarbanoyl)dodecahydro 1,4,7,9-tetraazaphenalene
Tetracyano ethylene
Pyrrole-2-carboxaldehyde
3-Isonicotinamido-4(3H)-quinazolinone
3-Pyridylmethylenemalononitrile
10(Dicyanomethylene)anthrone

Bis(beta naphthyl)fumarate
4-Pyridine carboxaldehyde
2,3-Dihydro-3-oxo-6-pyridazinylbenzoate
2(p-Chlorophenylacetylthio)-2-imidazoline
5-Benzylidenethiazolidine 2,4-dione
Benzaldehyde[p-(tricyanovinyl)phenyl]hydrazone
4-Methoxybenzaldehyde dimethylhydrazone
1,4-Bis(dicyanomethylene)cyclohexane
7,7,8,8-Tetracyano-p-quinodimethan
3-Cyanomethyl-4-cyano-5-aminopyrazole
p-Anisamidoxime
Tris(p-tolyl)phosphine
Bis(triphenylphosphine)nickel dithiocyanate
Bis(1-aziridinyl)phenyl phosphine sulfide
2,2-Dimethyl-1,3-propanediol cyclic sulfide
N-Furfurylphthalamic acid
Ethyl-2-cyano-3-(2-thienyl)acrylate
1,4-Bis(dimethylcarbamoyloxy)benzene
Carbohydrazide-N-carboxamide
Phenylisothiocyanate
Anisic acid hydrazide
Cyanoacetohydrazide
Cinnamylethyl carbonate
p-(Benzylxy)-alpha-2-hydroxyethylcinnamic acid gamma lactone